

terized for example by pressure surges in the apparatus.

The setting up of transition flow may for example be done by visual inspection and/or by measurement of the pressure difference Δp . Setting up transition flow by measuring the pressure difference Δp may be carried out for example by adjusting the rate of flow of gas through the bed (measured in parts by volume (STP) per unit time) and then gradually increasing the rate of flow, F , of liquid through the bed (measured in parts by volume per unit time) from a value l , in which the flow of liquid through the bed is predominantly laminar (i.e. the region of gas continuous flow), to a value t , in which the flow of liquid through the bed is predominantly turbulent (i.e. the region of transition flow), and in which the rate of change of pressure difference Δp with respect to changes in liquid flow rate, expressed as

$$\frac{d(\Delta p)}{dF},$$

is at least twice, preferably three times, that in the region of gas continuous flow. The value t of the rate of flow, F , of the liquid must not be too great or the region of pulsing flow will be entered, which is characterized by fluctuations in the pressure difference Δp caused by the pulses. The fluctuations have approximately the same frequency as the pulses. Visual adjustment of the transition flow conditions may be carried out, for example, in the manner described in A.I.Ch.E. Journal, Vol. 10 (1964) pp. 952—953. To this end, the conditions are adjusted such that the initial portion of the reactor downstream of the gas and liquid inlets is seen to contain an intimate mixture of gas and liquid in the form of a turbulent stream. Since the gas is consumed as the reaction proceeds, the number of gas bubbles in the reaction mixture decreases as the mixture flows through the reactor, the spaces formerly occupied by the consumed gas being filled by the liquid. Finally, it is seen that at the gas outlet of the reactor the amount of off-gas leaving the reactor in the form of bubbles in the liquid is only a fraction of the gas feed or may even be zero, depending on the percentage conversion of the gas or the proportion of inert gas mixed therewith.

To achieve the gas conversion required by the invention, it is necessary to use a long reaction vessel. Although the cross-section of the reactor may have any shape, for example a square or elliptical shape, cylindrical reactors are generally used. The length to diameter ratio of the reactor is generally from 5:1 to 300:1 and preferably from 10:1 to 150:1 and more particularly from 20:1 to 100:1. Instead of a single elongated reactor

having the l/d ratio specified above, two or more reactors may be connected in series, these reactors having a smaller l/d ratio than the said elongated reactor but producing a similar effect. Usually, two or more series-connected reactors will be used instead of a single elongated reactor when the use of the latter would present technical problems due to its length. The number of series-connected reactors used is usually from 2 to 10.

The reactors may be used in vertical or horizontal positions or, if desired, in inclined position. It is preferred, however, to use vertical reactors. The gas and liquid are passed downwardly through the reactors.

In gas/liquid reactions showing particularly high conversion rates of the gas, it may be advantageous not to pass the total amount of gas required to the initial portion of the elongated reactor, as this might easily cause pulsing flow conditions therein, but to divide the total amount of gas required into two or more partial streams which are fed to different points of the reactor along its axis. Where this method is adopted, the number of partial streams will usually be from two to about five, and where a number of reactors are connected in series, it will be convenient to feed the partial streams to the initial portions of each of the separate reactors. In this embodiment, the use of intermediate heat exchangers can achieve very uniform temperature conditions.

The process of the invention may be carried out batchwise or continuously. One method of continuous operation is to circulate the reaction mixture through the packed vessel, fresh starting materials being added to the circulated reaction mixture before it enters the reactor, whilst the reaction product is removed from the circulated reaction mixture after it has left the reaction zone. Continuous operation may also be effected by passing the reaction mixture through several, for example three or five, series-connected units.

When our new process is used for ethynylation reactions, i.e. the preparation of alkanols and alkyne diols by reacting acetylenes with aldehydes in the presence of heavy metal acetylides and optionally in the presence of basic agents, it is usual to use acetylides of heavy metals in group I or II of the Periodic Table as fixed-bed catalyst. When carrying out the reaction, the heavy metal acetylides may be used as such, or alternatively, the heavy metals themselves or salts thereof may be used, these being converted to the corresponding acetylides at the commencement of the reaction. Examples of suitable heavy metals are silver, gold, mercury and, in particular, copper. Where heavy metal salts are used, the nature of the anion is not critical. Examples of suitable heavy metal salts are copper phosphate, copper acetate, copper(I) chloride, copper(II) chloride, copper formate,

silver nitrate and mercury chloride. The metal acetylides are generally used on preformed supports, which also act as packing. Suitable carrier materials are, for example, aluminium oxide, animal charcoal, kieselguhr and, in particular, silica gel.

Ethynylation is conveniently carried out in the presence of an inert solvent or diluent such as an alcohol, ester, carboxamide, an aromatic or aliphatic hydrocarbon or water. As specific examples there may be mentioned ethanol, isobutanol, n-butanol, ethyl glycol, dioxane, tetrahydrofuran, dimethyl formamide and N-methylpyrrolidone. The reaction product itself or excess liquid starting material may be used as diluents, if desired.

Ethynylation is carried out using alkyl acetylenes, preferably those having from 3 to 6 carbon atoms, aryl acetylenes, preferably those having up to 12 carbon atoms, and alkenyl and alkynyl acetylenes preferably having from 4 to 6 carbon atoms, and, in particular, acetylene itself. As specific examples there may be mentioned methyl acetylene, ethyl acetylene, phenyl acetylene, vinyl acetylene and diacetylene.

Ethynylation is carried out using aromatic aldehydes preferably having up to 11 carbon atoms and, in particular, aliphatic aldehydes. The aliphatic aldehydes generally have from 1 to 12 carbon atoms and preferably from 1 to 6 carbon atoms. Examples of suitable aldehydes are acetaldehyde, butyraldehyde, n-capronaldehyde, benzaldehyde and, preferably, formaldehyde. The formaldehyde may be used in a monomeric form, for example as a commercial aqueous formaldehyde solution such as a 20—50% w/w solution, or in a polymeric form, for example in the form of trioxane or, in particular, in the form of para-formaldehyde. We prefer to use commercial aqueous formaldehyde solutions.

In general, the reaction is carried out without the addition of basic agents. However, ethynylation may be carried out in the presence of basic agents if desired. Suitable basic agents include carboxylic acid salts, carbonates and hydroxides of alkaline earth and alkali metals. As specific examples there may be mentioned potassium formate, sodium acetate, sodium carbonate, potassium carbonate, magnesium carbonate and calcium hydroxide. The basic agents may be used, for example, in solution in the reaction mixture.

In our new process, for example, the starting material with the lower boiling point is fed to the reactor as a gas and the starting material with the higher boiling point is introduced in liquid form. If an additional solvent is used, however, the higher boiling reactant may also form the gaseous phase or be included therein. The ethynylations are generally carried out at temperatures of between -10° and $+120^{\circ}\text{C}$, especially between -10° and $+100^{\circ}\text{C}$.

In general, the starting materials are reacted in a molar ratio of about 1:1. However, one of the starting materials may be used in excess if desired, in which case a convenient molar ratio of the starting materials is between 1:1 and 1:10, especially between 1:1 and 1:3.

When our new process is applied to catalytic hydrogenations, use may be made of conventional fixed-bed hydrogenation catalysts such as platinum, palladium, rhodium, ruthenium, nickel and cobalt metals conveniently supported on animal charcoal, barium sulfate, calcium carbonate, silica gel or alumina. The process of the invention may be used for carrying out conventional catalytic hydrogenations, for example the hydrogenation of carbon-carbon triple bonds to corresponding double bonds or saturated bonds, the hydrogenation of double bonds, the hydrogenation of aromatic hydrocarbons to cycloaliphatic hydrocarbons, of carbonyl groups to hydroxyl groups, of nitro groups to amino groups, of nitrile compounds to amines or of amino-oxide groups to amines, the hydrogenolysis of protective groups such as benzyl ester or benzyl ether groups, the hydrogenolysis of acid chlorides to aldehydes and the hydrogenating amination of aldehydes or ketones and other reactions.

The hydrogenation may be carried out in the absence of solvents. Alternatively however, the hydrogenation may be carried out in the presence of the liquids normally used in catalytic hydrogenations, such as ethers, esters, lower aliphatic carboxylic acids, alcohols or water. Catalytic hydrogenation carried out by the method of the invention may be effected at temperatures of, say, between 10° and 300°C and pressures of, say, between atmospheric pressure and 325 atmospheres. If desired, however, subatmospheric pressure, for example a pressure of 600 mm of Hg, may be used.

EXAMPLE 1

The reaction is carried out using a pressure-resistant packed column (1) of stainless steel and having a length of 6 m and an internal diameter of 45 mm (see Figure 2). The column is packed with supported catalyst in the form of pellets of 3 mm in diameter and from 2.5 to 5 mm in length, which catalyst contains, on analysis, 85% by weight of silica gel, 12% by weight of CuO and 3% by weight of bismuth. A 37% by weight aqueous formaldehyde solution (11) is fed through line (11a) at a rate of 1 litre per hour (1/hr), and acetylene (9) is fed through line (9a) at a rate of 120 l/hr (STP). The circulated reaction liquid is fed to the packed column through feed line (12). The reaction mixture leaving the packed column is separated in the separator (2) to give a gas phase and a liquid reaction mixture. The liquid reaction mixture is recycled to the packed column from the

separator through a withdrawal line (16), a circulating pump (3), a flowmeter (6) and a cooler (5), at a rate of 92 l/hr. A portion of the liquid reaction mixture is withdrawn from the separator (2) via the discharge line (14) as reaction product (15). Off-gas (10) is removed through the withdrawal line (10a) at a rate of 30 l/hr (STP). The pressure differential between the gas feed to the column and the off-gas is measured by a pressure differential gage (8) and is 0.3 atmospheres gage. At an acetylene pressure of 5 atmospheres gage, the reaction temperature in the packed column is 105°C. Reaction product (15) is withdrawn from the separator at a rate of 1.17 l/hr, the content of formaldehyde therein being 15% by weight. The yield of butynediol on formaldehyde consumed is 97% of theory. Formaldehyde conversion is 60%.

EXAMPLE 2

Five vertical packed columns each having a length of 8 m and an internal diameter of 140 mm are series-connected by pipes such that the bottom of the first reactor is connected to the top of the second reactor, the bottom of the second reactor is connected to the top of the third reactor and so on.

The gas/liquid mixture leaving the bottom of a reactor is thus passed to the top of the next reactor without separation. A separator is provided at the end of the final reactor. Each of the five columns is packed with a hydrogenation catalyst consisting of 20% nickel-on-silica gel pellets of 6 mm in diameter and from 4 to 10 mm in length.

2 - Ethylhexanol - 1 is circulated through the five columns at a rate of 960 l/hr and 2 - ethylhexane - 2 - al - 1 is metered to the top of the first packed column at a rate of 160 l/hr. The temperature of the feed is 90°C. Hydrogen is also passed to the top of the first column at a rate of 44 mm³/hr (STP) and at a pressure at 27 atmospheres gage. The gas and liquid passed downwardly through each of the five columns are separated from each other on leaving the fifth column. Reaction product is removed from the liquid circulation at a rate of 162 l/hr. The gas leaving the final column at the rate of 5.5 m³/hr (STP) is discarded as off-gas. The product leaving the final column has a temperature of 170°C. The mixture returned to the first column is cooled to 120°C. The 2 - ethylhexanol - 1 leaving the final column is 96% pure. The yield is 97.7%.

EXAMPLE 3

A glass tube having an internal diameter of 30 mm and a length of 2 m is packed with a hydrogenation catalyst consisting of 0.4% by weight of palladium and 99.6% by weight of silica gel in the form of pellets having a diameter of 2 mm and a length of from 2

to 6 mm. A 20% w/w solution of trimethyl - p - benzoquinone in isobutanol is pumped to the top of the vertical column through a line at the rate of 1.2 l/hr, hydrogen being passed through another line at the rate of 50 l/hr (STP). The bottom of the tube is connected to a vessel in which the gas/liquid mixture leaving the tube separates. The liquid is recycled to the top of the reaction tube by a pump, a portion thereof being withdrawn from the separator at the same rate as that at which fresh quinone solution is introduced. Liquid is circulated at a rate of 56 l/hr. The difference in pressure between the top and bottom of the column is 55 mm Hg. The temperature of the circulated liquid is 85°C. Off-gas is allowed to leave the separator at the end of the tube at the rate of 1.5 l/hr (STP). Reaction solution is withdrawn from the separator at the rate of 1.2 l/hr, the content of trimethylhydroquinone therein being 20% by weight. Both conversion and yield are virtually 100% of theory.

Relationship Between Pressure Differential Δp and the Rate of Liquid Feed F to the Packing in the Packed Column

Measurement of the relationship between the pressure differential Δp and the rate of liquid feed F to the packing in the packed column is effected using the following apparatus (see Figure 3): a glass tube (1) having a length of 130 cm and an internal diameter of 45 mm is filled to a height of 120 cm with glass spheres of 3 mm in diameter. The glass spheres are retained at the bottom of the column by a sieve having a mesh width of 1.5 mm. The outlet has a cross-sectional area which is larger than the total cross-sectional area of the free spaces between the spheres, so that no additional pressure may result from a damming effect of the outlet on the gas/liquid mixture. The rates of flow of the gas and liquid are measured by rotameters (7) and (6) respectively, the pressure differential Δp being measured by the manometer (8). The latter measurement is carried out by maintaining a constant rate of flow of hydrogen (9) and slowly raising the rate of flow F of the liquid (water). The relationship between the pressure differential Δp and the rate of liquid flow F at different rates of gas flow (kept constant in any one series of experiments) is shown in Figure 1.

WHAT WE CLAIM IS:—

1. A process for carrying out an exothermic reaction between a gas and a liquid in the presence of a catalytic fixed bed, comprising passing the gas and the liquid concurrently downwardly through a reactor containing the fixed bed and downwardly through the fixed bed so as to cause a pressure difference Δp to be set up between the upper and lower

ends of the bed, and controlling the rate of the reaction so as to maintain the ratio of the rate by volume of gas fed to the bed to the rate by volume 3 of off gas produced from the reaction, after correcting to N.T.P. at from 4:1 to 100:1, the gas fed to the bed being at least partly consumed during the reaction and the rate of flow, F, of the liquid through the bed being at such a value t that, at a constant rate of feeding the gas to the bed, the change of pressure difference Δp with respect to changes in liquid flow rate, i.e.

$$\frac{d(\Delta p)}{dF},$$

is at least twice as great when F equals t as when F equals 1, 1 being a liquid flow rate which causes at least predominantly laminar flow of the liquid through the bed, and the value t not being great enough to cause pulsing of pressure difference Δp .

2. A process as claimed in claim 1 wherein the reactor is of elongate shape.

3. A process as claimed in claim 2, wherein the elongate reactor is formed by two or more separate reactors connected in series.

4. A process as claimed in claim 1 or 2, wherein the total gas feed is divided into two or more partial streams which are fed to the reactor at different points along its axis.

5. A process as claimed in claim 3, wherein a partial stream of the total gas feed is fed to each of the separate reactors.

6. A process as claimed in any of claims 1 to 5 wherein the ratio by volume of the gas feed to the off-gas is maintained at from 5:1 to 20:1.

7. A process as claimed in any of claims 1 to 6 wherein the gas reactant is employed in a commercially pure form.

8. A process as claimed in any of claims 1 to 7 wherein the reaction is carried out in one or more reactors having an overall length: diameter ratio of from 20:1 to 100:1.

9. A process as claimed in any of claims 1 to 8 wherein the reaction is carried out in a narrow temperature range having a range of variation not exceeding $\pm 20^\circ\text{C}$.

10. A process as claimed in any of claims 1 to 9 wherein the reaction is the ethynylation of an aldehyde with an acetylene in the presence of a heavy metal acetylide as catalyst carried on a support.

11. A process as claimed in any of claims 1 to 10 wherein the reaction is the catalytic hydrogenation of an organic compound in the presence of a hydrogenation catalyst.

12. A process for carrying out gas/liquid exothermic reactions in the presence of a catalytic fixed bed as claimed in claim 1 and substantially as described in any of the foregoing Examples.

J. Y. & G. W. JOHNSON,
Furnival House,
14—18, High Holborn,
London, WC1V 6DE.
Chartered Patent Agents,
Agents for the Applicants.

